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# REDUCTION BY A MODEL OF NAD(P)H. 42. DIRECT EVIDENCE FOR ONE ELECTRON TRANSFER MECHANISM IN THE REDUCTION OF ARENEDIAZONIUM SALTS

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*Summary*: Arenediazonium salts are reduced by an NAD(P)H-model in methanol at room temperature to afford the corresponding reduction product, ArH. The reaction proceeds partially with a radical-chain mechanism involving initial one electron transfer from the NAD(P)H-model to the diazonium salt.

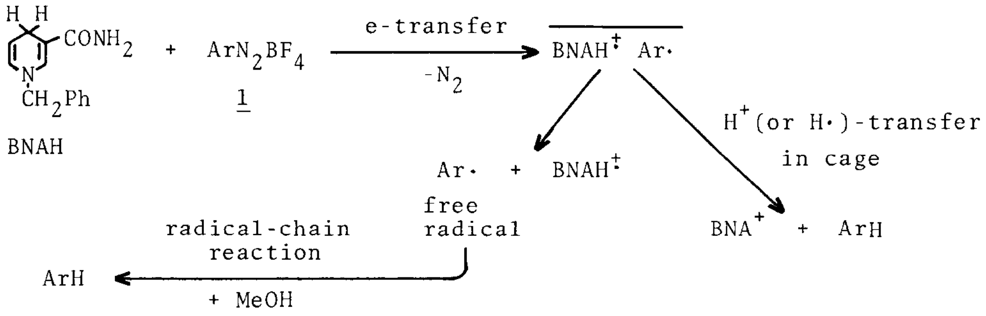
Although one electron transfer prior to a proton (or a hydrogen atom) transfer has been suggested in the reduction of many substrates with an NAD(P)H-model based on kinetics (*1*) and product analyses (*2*), information for intrinsic ability of an NAD(P)H-model to initiate a radical-chain reaction has been little available. In a preliminary work, it was found that an NAD(P)H-model reduces bromotrichloromethane to chloroform with a radical-chain mechanism (*3*). Unfortunately, the work failed to decide whether the reaction is initiated only by the NAD(P)H-model. Recently, Shinkai *et al*. reported the polymerization of acrylamide initiated by an NAD(P)H-model(*4*). This system, however, seems to be elaborated. Thus, we have been looking for a simpler system and found that an NAD(P)H-model, N-benzyl-1,4-dihydronicotinamide (BNAH), initiates radical-chain reaction in the dediazoniation of arenediazonium fluoroborates($ArN_2BF_4$:1a, Ar = *p*-$CH_3$-$C_6H_4$;1b, Ar = *p*-Br-$C_6H_4$;1c, Ar = *p*-$NO_2$-$C_6H_4$) in methanol at room temperature.

It has been well known that thermal dediazoniation of 1c in acidic methanol affords a reduction product, nitrobenzene (2c),whereas 1a is dediazoniated under a similar condition forming practically only *p*-methoxyanisole, instead of the reduction product, toluene (2a), and that in the dediazoniation of 1b, both reduction and substitution take place affording *p*-bromobenzene (2b) and *p*-bromoanisole, respectively. The yield of 2b is supressed by the presence of oxygen (*5-7*). The results from experiments with radical-initiators and radical-inhibitors have revealed that the reduction product and ether are formed *via* a radical-chain path and an ionic one, respectively (*7*).

When we examined the reaction of 6.0 x $10^{-2}$ mmole of 1a-c with appropriate amount of BNAH in 3 ml (for 1a-b) or 5 ml (for 1c) of methanol at room temperature in the dark, formation of the corresponding reduction products, 2a-c, was observed on G.L.C. within a few minutes (silicon SE column; *p*-xylene, *p*-methylanisole, and *m*-dimethoxybenzene as internal standards for 2a, 2b, and 2c, respectively). No other product was detectable. On the other hand, in the absence of BNAH, 1a-c did not afford any product in detectable amount. Thus, self-decompositions of 1a-c were not observed within the reaction period. The yields of 2a-c were dependent upon the ratio of initial amount of BNAH to those of 1a-c, but not upon the concentrations of the starting materials within the range employed in the present work.

As illustrated in Figure 1, the amounts of 2a-c produced under nitrogen atmosphere were larger than the stoichiometric one of BNAH. A radical-chain inhibitor, oxygen or N-*t*-butyl-α-phenylnitrone, lowered the yields of 2a-c. Moreover, the reaction in methanol-$d_4$ gave deuterated reduction products, the yields of which were analyzed on a GC-MS (Table 1). These facts indicate unambiguously the major role of a radical-chain path in the course of the reaction.

Direct "hydrogen" transfer from BNAH to 1a-c in a solvent-cage as a simultaneous process, however,is the other candidate because deuterium incorporation into the product is not quantitative. Since no decomposition takes place without BNAH and the radical-chain reaction does occur in the presence of BNAH, the trigger for dediazoniation of 1a-c might be one electron transfer from BNAH to 1a-c,which may accompany the delivery of nitrogen molecule as have been known in thermal dediazoniation of certain arenediazonium salts in the presence of an acid (*8*) or a one electron donor (*9*). In fact, rigorous bubbling was recognized immediately after the mixing of a solution of BNAH with 1a-c. Then, the generated aryl radical would accept a proton (or a hydrogen atom) from the cation radical of BNAH within the cage of solvent, or would escape from the cage



Scheme 1

to undergo well-known radical-chain reaction abstracting a hydrogen atom from the solvent (*8*,*9*). Conversion of methanol to formaldehyde in such a radical-

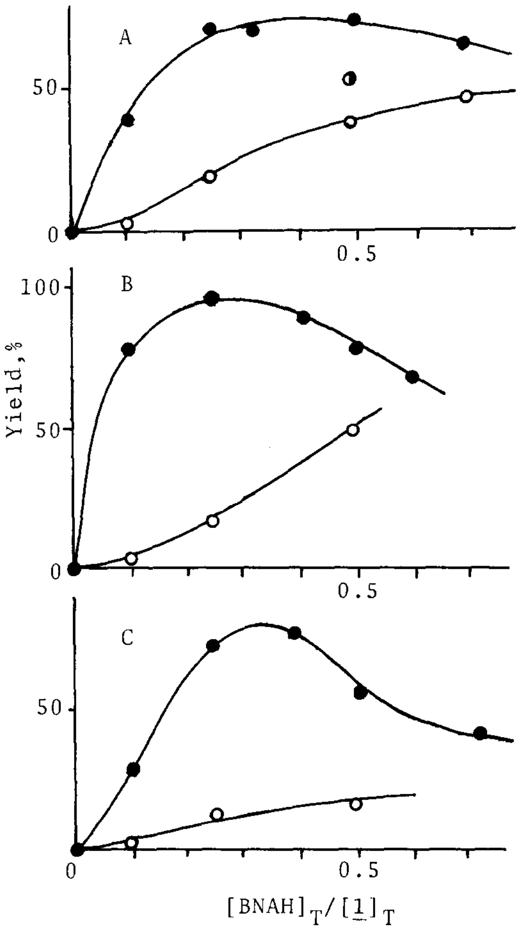


Figure 1. Yields of 2 varying the initial amount of BNAH[a)]

a) A, B, and C represent the runs for 1a, 1b, and 1c, respectively. Reaction time; 10 min. ● and ○ ; Yields of 2 based on 1 under $N_2$ and $O_2$ atmospheres, respectively. ◑;Yield of 2a based on 1a in the presence of N-*t*-butyl-α-phenylnitrone (0.85 x $10^{-2}$ mmole).

Table 1. Yields of Non-Deuterated and Deuterated Products Based on 1 in the Reaction in Methanol-$d_4$[a)]

| Compd. | Atmosphere | | | | | |
|---|---|---|---|---|---|---|
| | $N_2$ | | | $O_2$ | | |
| | H[b)] | D[c)] | D/H[d)] | H[b)] | D[c)] | D/H[d)] |
| 2a | 27% | 48% | 1.8 | 23% | 16% | 0.7 |
| 2b | 18 | 62 | 3.4 | 14 | 36 | 2.6 |
| 2c | 8 | 57 | 7.1 | 6 | 14 | 2.3 |

a) In 0.5 ml of $CD_3OD$ at room temperature in the dark. Reaction time; 10 min. 1;1.5 x $10^{-2}$ mmole. BNAH;0.75 x $10^{-2}$ mmole. b) Yield of non-deuterated product, ArH. c) Yield of deuterated product, ArD. d) Ratio of yields of deuterated to non-deuterated products.

chain reaction is also well-known (Scheme 1). Interestingly, the similar but stoichiometric reaction takes place in the presence of an amine such as triethylamine in place of BNAH.

In the reactions in methanol-$d_4$, deuterated and non-deuterated products would be formed *via* radical-chain and in-cage "hydrogen" transfer reactions, respectively. In spite of uncertainty of the length of radical-chain, there remains no doubt that the more favorable the radical-chain process, the larger the yield of deuterated product is. Therefore, the ratio of deuterated product to non-deuterated one can be an index of the favorability of radical-chain process, although it is in an arbitrary scale. Thus, Table 1 shows the order of the favorability of radical-chain process to be 1a < 1b < 1c under nitrogen atmosphere when $[BNAH]_T/[1]_T$ is 0.5, which is in accordance with the fact that, of thermal dediazoniations of 1a-c in acidic methanol, the radical-chain process with 1c and that with 1a are most and least favorable, respectively (*8*). Under oxygen atmosphere, on the other hand, the ratio for 2c is unexpectedly small. Such a small ratio may be due to experimental errors arising from very poor yield of 2c. The order similar to that under anaerobic condition might also appear under oxygen atmosphere. Moreover, for 2a-c, the yields of non-deuterated products under nitrogen and oxygen atmospheres are practically the same (compare the first column with the fourth column in Table 1), respectively, which indicates that oxygen would affect only radical-chain process, as predicted above. The decrease in yields of 2a-c with the increase in the amount of BNAH after the maximum seems to be the result that excess BNAH plays an inhibitory role.

Thus, it is concluded that BNAH reduces 1 to 2 in a manner that the former transfers one electron to the latter in the initiation of the reaction. BNAH thus acts as a free-radical initiator in the dediazoniation of 1. Moreover, this result would point out the importance of the initial one electron transfer step in the reduction by an NAD(P)H-model in general. Studies on the more detailed mechanism are in progress in our laboratories.

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